

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 945 162 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.09.1999 Bulletin 1999/39

(51) Int. Cl.⁶: **B01D 53/14**

(21) Application number: **99105774.6**

(22) Date of filing: **22.03.1999**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **23.03.1998 JP 7365898**

(71) Applicant:
**Mitsubishi Heavy Industries, Ltd.
Tokyo 100-0005 (JP)**

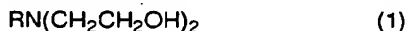
(72) Inventors:
• **Iijima, Masaki,
c/o Mitsubishi Heavy Ind., Ltd
Chiyoda-ku, Tokyo (JP)**

• **Mitsuoka, Shigeaki,
c/o Hiroshima R. & D. Center
Nishi-ku, Hiroshima-shi, Hiroshima-ken (JP)**
• **Tanaka, Hiroshi,
c/o Hiroshima R. & D. Center
Nishi-ku, Hiroshima-shi, Hiroshima-ken (JP)**

(74) Representative:
**Behrens, Dieter, Dr.-Ing. et al
Wuesthoff & Wuesthoff
Patent- und Rechtsanwälte
Schweigerstrasse 2
81541 München (DE)**

(54) Process and system for the removal of carbon dioxide present in gases

(57) This invention relates to a process for the removal of carbon dioxide present in gases which includes the step of bringing a carbon dioxide-containing gas into contact with an aqueous solution containing, as an absorbent, at least one amine compound of the general formula (1)



wherein R represents an alkyl group of 2 to 4 carbon atoms, or an aqueous solution containing both at least one amine compound of the above general formula (1) and at least one other amine compound, as well as a system therefor.

This invention can provide a process for the removal of carbon dioxide present in gases by use of an absorbing fluid containing an absorbent having higher CO₂-absorbing power and CO₂-releasing power and being more advantageous from the viewpoint of energy efficiency, as compared with the conventionally used absorbing fluid.

EP 0 945 162 A1

Description

FIELD OF THE INVENTION AND RELATED ART STATEMENT

[0001] This invention relates to a process for the removal of carbon dioxide (CO₂) present in CO₂-containing gases, and a system therefor. More particularly, it relates to a process for the removal of carbon dioxide present in a gas having a CO₂ partial pressure within a predetermined range wherein the removal of carbon dioxide is effected by gas-liquid contact with high energy efficiency, and a system therefor.

[0002] Conventionally, investigations have been made on the removal and recovery of CO₂ having a partial pressure in the range of about 0.3 to 50 atmospheres (atm.), from various industrial gases such as natural gas and synthesis gases, and a variety of processes therefor have been proposed.

[0003] For example, in a process for reacting and absorbing carbon dioxide by gas-liquid contact, an aqueous solution of N-methyldiethanolamine (MDEA) with or without an absorption accelerator (e.g., piperazine) has been used in most cases.

[0004] However, the above-described process for the removal of CO₂ by using an aqueous solution of MDEA has the disadvantage that, when the aqueous solution is used in the usual partial pressure range, the released CO₂ level is not sufficient to achieve the efficient removal of carbon dioxide.

[0005] More specifically, in order to remove carbon dioxide from an object gas to be treated, for example, by gas-liquid contact, it is desirable that, with respect to an aqueous solution containing an absorbent (i.e., an absorbing fluid), the difference between the saturated CO₂ level under the conditions of the absorption region and the saturated CO₂ level under the conditions of the regeneration region is as great as possible. However, the aforesaid conventional absorbing fluid cannot be said to have sufficient power in the respect. Accordingly, a more advantageous process has been desired not only from this point of view, but also from the viewpoint of energy efficiency.

OBJECT AND SUMMARY OF THE INVENTION

[0006] In view of the above-described problem, the present inventors made an intensive investigation for the purpose of developing a process for the removal of carbon dioxide present in gases by use of an absorbing fluid containing an absorbent having higher CO₂-absorbing power and CO₂-releasing power and being more advantageous from the viewpoint of energy efficiency, as compared with the conventionally used absorbing fluid comprising an aqueous solution of MDEA.

[0007] As a result, the present inventors have found that the above-described problem can be solved, for example, by bringing a carbon dioxide-containing gas into contact with an aqueous solution containing a specific amine compound as an absorbent.

[0008] The present invention has been completed from this point of view.

[0009] Accordingly, the present invention provides a process for the removal of carbon dioxide present in gases which includes the step of bringing a carbon dioxide-containing gas into contact with an aqueous solution containing, as an absorbent, at least one amine compound of the general formula (1)



wherein R represents an alkyl group of 2 to 4 carbon atoms.

[0010] Moreover, the present invention also provides a process for the removal of carbon dioxide present in gases which includes the step of bringing a carbon dioxide-containing gas into contact with an aqueous solution containing both at least one amine compound of the above general formula (1) and at least one other amine compound having carbon dioxide-absorbing power.

[0011] Furthermore, the present invention also provides a system suitable for carrying out the above-described processes of the present invention.

[0012] According to the processes of the present invention, carbon dioxide present in a gas having a CO₂ partial pressure in the range of about 0.3 to 50 atm (absolute pressure) can be absorbed and recovered with higher energy efficiency, as compared with conventional processes using MDEA.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

FIG.1 is a flow diagram of an exemplary system for carrying out the process for the removal of carbon dioxide from gases in accordance with the present invention.

[0014] The reference numerals given in this figure are defined as follows: 1, object gas to be treated; 2, absorption tower; 3, treated gas; 4, CO₂-rich absorbing fluid; 5, heat exchanger; 6, flash drum; 7, regeneration tower; 8, first regenerated CO₂-lean absorbing fluid; 9, second regenerated CO₂-lean absorbing fluid; 10, reboiler; 11, overhead condenser; 12, separating drum; 13, recirculation fluid; 14, nozzle; 15 and 16, released CO₂; and 17, steam source.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0015] One embodiment of the present invention is described hereinbelow with reference to the accompanying drawing (FIG.1).

[0016] According to the present invention, a carbon dioxide-containing gas is brought into contact with an aqueous solution containing, as an absorbent, at least one amine compound of the general formula (1)



wherein R represents an alkyl group of 2 to 4 carbon atoms, or an aqueous solution containing both at least one amine compound of the above general formula (1) and at least one other amine compound having carbon dioxide-absorbing power.

[0017] The amine compound used as the absorbent in the present invention is represented by the above general formula (1).

[0018] In this formula, R represents an alkyl group of 2 to 4 carbon atoms. Specific examples of the alkyl group of 2 to 4 carbon atoms include ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl and tert-butyl groups. Among others, it is especially preferable to use N-ethyldiethanolamine in which R is an ethyl group.

[0019] As to the aqueous solution (or absorbing fluid) containing the aforesaid absorbent and used for contact with a carbon dioxide-containing gas, the concentration of the aforesaid absorbent is usually in the range of 15 to 65% by weight and preferably 30 to 50% by weight. Moreover, when brought into contact with the gas, the absorbing fluid usually has a temperature in the range of 30 to 70°C and preferably 35 to 60°C.

[0020] If necessary, the aforesaid absorbing fluid used in the present invention may contain a corrosion inhibitor, a deterioration inhibitor and the like.

[0021] Moreover, in order to further enhance the CO₂-absorbing power of the aforesaid absorbing fluid (e.g., the absorbed CO₂ level and the absorption rate), one or more other amine compounds having CO₂-absorbing power may be used in admixture with the amine compound of the above general formula (1). Preferred examples of such other amine compounds include monoethanolamine, 2-methylaminoethanol, 2-ethylaminoethanol, 2-n-propylaminoethanol, 2-isopropylaminoethanol, 2-n-butylaminoethanol, piperazine, 2-methylpiperazine, 2,5-dimethylpiperazine and 2-piperidineethanol. When such other amine compounds are used, the concentration of them alone is usually in the range of 1.5 to 50% by weight and preferably 5 to 40% by weight, provided that they are soluble in water together with the amine compound of the above general formula (1).

[0022] The object gas to be treated in the present invention is one having a CO₂ partial pressure in the range of 0.3 to 50 atm. (absolute pressure), and specific examples thereof include various industrial gases produced or dealt with in chemical plants, such as natural gas and synthesis gases.

[0023] Although no particular limitation is placed on the system which can be employed to carry out the process of the present invention, one specific example thereof is described below with reference to FIG. 1. In this figure, only essential elements are shown.

[0024] In FIG.1, reference numeral 1 designates an object gas to be treated; 2, an absorption tower; 3, treated gas; 4, a CO₂-rich absorbing fluid; 5, a heat exchanger which is installed as required; 6, a flash drum; 7, a regeneration tower; 8, a first regenerated CO₂-lean absorbing fluid; 9, a second regenerated CO₂-lean absorbing fluid; 10, a reboiler; 11, an overhead condenser; 12, a separating drum; 13, a recirculation fluid; 14, a nozzle; and 15 and 16, released CO₂.

[0025] A gas 1 having a CO₂ partial pressure in the range of 0.3 to 50 atm. (i.e., an object gas to be treated) is fed to the lower part of an absorption tower 2. This absorption tower 2 is packed, for example, with a wetted-wall type packing material so that the ascending gas will come into efficient gas-liquid contact with a CO₂-lean absorbing fluid fed to the upper part thereof. The treated gas 3 having been freed of carbon dioxide by contact with the CO₂-lean absorbing fluid is discharged from the top of absorption tower 2.

[0026] On the other hand, the CO₂-lean absorbing fluid having absorbed CO₂ turns into a CO₂-rich absorbing fluid 4, which is withdrawn from the bottom of absorption tower 2 by means of a pump, transferred to a regeneration step, and regenerated therein.

[0027] The regeneration step consists essentially of a flash drum 6 and a regeneration tower 7. In operation, the use of flash drum 6 alone, the use of both flash drum 6 and regeneration tower 7, or the use of regeneration tower 7 alone is suitably chosen according to the type of the absorbent and the treating conditions.

[0028] For example, when flash drum 6 alone is used, CO₂-rich absorbing fluid 4 having a pressure higher than

atmospheric pressure is introduced into flash drum 6 which is preset at atmospheric pressure or in the vicinity thereof (e.g., atmospheric pressure \pm 0.5 atm). Thus, CO₂-rich absorbing fluid 4 is flashed to release some CO₂. The released CO₂ 15 is discharged from the top of flash drum 6.

[0029] The absorbing fluid having a reduced CO₂ content as a result of the release of some CO₂ (i.e., a first regenerated CO₂-lean absorbing fluid 8) is directly recycled to absorption tower 2 and reused therein.

[0030] Alternatively, when both flash drum 6 and regeneration tower 7 are used according to the type of the absorbent, the treating conditions, and the like, part of the aforesaid first regenerated CO₂-lean absorbing fluid 8 is introduced into a regeneration tower 7.

[0031] The lower part of regeneration tower 7 is equipped with a reboiler 10 using a steam source 17, so that CO₂ is released from first regenerated CO₂-lean absorbing fluid 8 by steam stripping. The released CO₂, together with steam, is discharged from the top of regeneration tower 7, cooled with an overhead condenser 11, and then introduced into a separating drum 12 where it is separated into the released CO₂ 16 and the condensate. The released CO₂ 16 is discharged out of the system, while the condensate is recirculated to a nozzle 14 of regeneration tower 7 as a recirculation fluid 13.

[0032] The regenerated absorbing fluid (i.e., a second regenerated CO₂-lean absorbing fluid 9) is withdrawn from the bottom of regeneration tower 7 and recycled for use in the absorption step together with first regenerated CO₂-lean absorbing fluid 8. In the case of the absorbing fluid from which only a small amount of CO₂ is released in flash drum 6, the CO₂-rich absorbing fluid may be directly regenerated in regeneration tower 7, instead of being passed through flash drum 6 (the line used for this purpose is omitted in FIG. 1).

[0033] The present invention makes it possible to remove carbon dioxide from gases by use of an absorbing fluid having higher CO₂-absorbing power and being more advantageous from the viewpoint of energy efficiency, as compared with the conventionally used absorbing fluid comprising an aqueous solution of MDEA.

[0034] That is, according to the process of the present invention, carbon dioxide present in a gas having a CO₂ partial pressure in the range of about 0.3 to 50 atm. (absolute pressure) can be absorbed and recovered with higher energy efficiency, as compared with conventional processes using an absorbent comprising MDEA or the like. Thus, the present invention provides a CO₂ absorption process which is very valuable from the viewpoint of energy saving and hence has a very important significance from an industrial point of view.

[0035] The present invention (in particular, the absorbing fluid used therein) is more specifically explained with reference to the following examples. However, these examples are not to be construed to limit the scope of the invention.

Example 1

[0036] An aqueous solution containing 3 moles/liter (or 40% by weight) of N-ethyldiethanolamine (EDEA) as an absorbent was used as an absorbing fluid. In a stainless steel reactor of double-tube structure, the inner tube (with a capacity of 2 liters) was charged with 500 milliliters of the absorbing fluid, and its temperature was kept constant by passing a temperature-controlled heating medium (silicone oil) through the outer tube.

[0037] The absorbing fluid was circulated through the reactor by raising the absorbing fluid from the lower part to the upper part of the reactor through an absorbing fluid circulation line having a pump installed therein, and allowing it to flow downward. On the other hand, CO₂ gas was fed from a cylinder to the lower part of the reactor. At the same time, the unabsorbed CO₂ was discharged from the reactor through a CO₂ discharge line having an automatic regulating valve installed therein so as to maintain a constant CO₂ partial pressure within the reactor. Thus, the CO₂ partial pressure was kept constant.

[0038] After starting the feed of CO₂ gas, samples of the absorbing fluid were taken at regular intervals of time and their CO₂ contents were measured with a CO₂ analyzer (or total organic carbon meter) to calculate the saturated CO₂ level (in moles of CO₂ per mole of amine).

[0039] The above-described procedure was carried out under the conditions ① of the absorption region (including a CO₂ partial pressure of 10 atm. and a temperature of 40°C) and the conditions ② of the regeneration region (or steam stripping) (including a CO₂ partial pressure of 0.1 atm. and a temperature of 120°C), and the corresponding saturated CO₂ levels (in moles of CO₂ per mole of amine) were calculated. Moreover, the released CO₂ level (A-B) was calculated from the difference between the saturated CO₂ level (A) under the conditions ① of the absorption region and the saturated CO₂ level (B) under the conditions ② of the regeneration region.

[0040] The results thus obtained are shown in Table 1.

Example 2

[0041] An experiment was carried out in the same manner as in Example 1, except that an aqueous solution containing 3 moles/liter (or 48% by weight) of N-n-butyldiethanolamine (BDEA) as an absorbent was used as an absorbing fluid, in place of the aqueous solution containing 3 moles/liter (or 40% by weight) of N-ethyldiethanolamine (EDEA) as

an absorbent. Then, the saturated CO₂ levels (in moles of CO₂ per mole of amine) under aforesaid conditions ① and ② and the released CO₂ level were calculated in the same manner as in Example 1.

[0042] The results thus obtained are shown in Table 1.

Comparative Example 1

[0043] An experiment was carried out in the same manner as in Example 1, except that an aqueous solution containing 3 moles/liter (or 36% by weight) of N-methyldiethanolamine (MDEA) as an absorbent was used as an absorbing fluid, in place of the aqueous solution containing 3 moles/liter (or 40% by weight) of N-ethyldiethanolamine (EDEA) as an absorbent. Then, the saturated CO₂ levels (in moles of CO₂ per mole of amine) under aforesaid conditions ① and ② and the released CO₂ level were calculated in the same manner as in Example 1.

[0044] The results thus obtained are shown in Table 1.

Table 1

	Absorbent	Saturated CO ₂ level (A) under conditions ① (moles of CO ₂ /mole of amine)	Saturated CO ₂ level (B) under conditions ② (moles of CO ₂ /mole of amine)	Released CO ₂ level (A-B) (moles of CO ₂ /mole of amine)
Example 1	EDEA	0.951	0.029	0.922
Example 2	BDEA	0.884	0.014	0.870
Comparative Example 1	MDEA	0.884	0.030	0.854

[0045] It is evident from the results shown in the above Table 1 that, when an aqueous solution of N-ethyldiethanolamine (EDEA) that is an amine compound in accordance with the present invention is used as an absorbing fluid for CO₂ gas (Example 1), the saturated CO₂ level per mole of the absorbent in the absorption region (conditions ①) is increased as compared with the case in which an aqueous solution of MDEA is used (Comparative Example 1). Consequently, it can be seen that the released CO₂ level becomes higher than in the case in which an aqueous solution of MDEA is used, thus making it possible to remove CO₂ more efficiently.

[0046] It is also evident from the results shown in the above Table 1 that, when an aqueous solution of N-n-butyldiethanolamine (BDEA) that is an amine compound in accordance with the present invention is used as an absorbing fluid for CO₂ gas (Example 2), the saturated CO₂ level per mole of the absorbent in the regeneration region (conditions ②) is decreased as compared with the case in which an aqueous solution of MDEA is used (Comparative Example 1). Consequently, it can be seen that the released CO₂ level becomes higher than in the case in which an aqueous solution of MDEA is used, thus making it possible to remove CO₂ more efficiently.

Claims

1. A process for the removal of carbon dioxide present in gases which includes the step of bringing a carbon dioxide-containing gas into contact with an aqueous solution containing, as an absorbent, at least one amine compound of the general formula (1)



wherein R represents an alkyl group of 2 to 4 carbon atoms.

2. A process for the removal of carbon dioxide present in gases which includes the step of bringing a carbon dioxide-containing gas into contact with an aqueous solution containing both at least one amine compound of the above general formula (1) and at least one other amine compound having carbon dioxide-absorbing power.
3. A process for the removal of carbon dioxide present in gases as claimed in claim 1 or 2 wherein, in the above general formula (1), R is an ethyl group.
4. A process for the removal of carbon dioxide present in gases as claimed in claim 1 or 2 wherein said aqueous solution contains the absorbent of the above general formula (1) at a concentration in the range of 15 to 65% by weight.

EP 0 945 162 A1

5. A process for the removal of carbon dioxide present in gases as claimed in claim 1 or 2 wherein, when brought into contact with said gas, said aqueous solution containing the absorbent of the above general formula (1) has a temperature in the range of 30 to 70°C.

6. A system for the removal of carbon dioxide which includes an absorption tower for bringing a carbon dioxide-containing gas into gas-liquid contact with an aqueous solution containing, as an absorbent, at least one amine compound of the general formula (1)

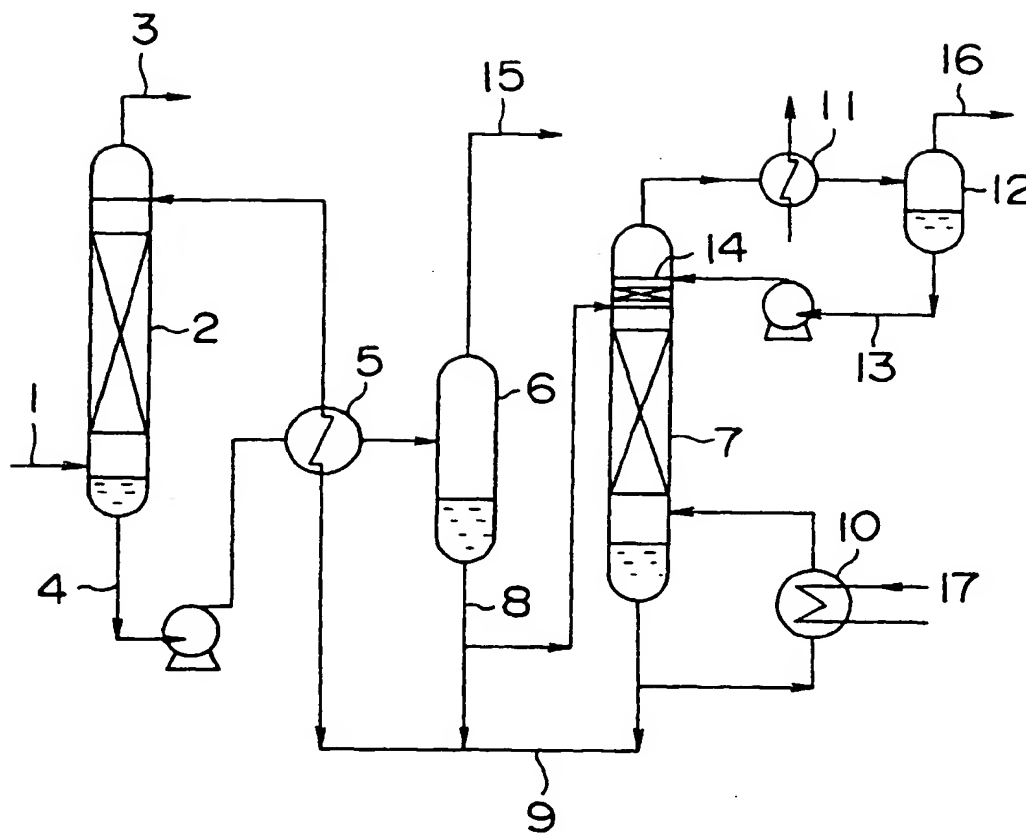


wherein R represents an alkyl group of 2 to 4 carbon atoms.

7. A system for the removal of carbon dioxide as claimed in claim 6 which further includes regeneration means for regenerating said aqueous solution having absorbed carbon dioxide in said absorption tower.

8. A system for the removal of carbon dioxide as claimed in claim 7 wherein said regeneration means comprises a flash drum or a regeneration tower, or both.

FIG. 1





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 10 5774

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 558 019 A (KANSAI ELECTRIC POWER CO ; MITSUBISHI HEAVY IND LTD (JP)) 1 September 1993 * page 3, line 1-5 * * page 5, line 32 - page 6, line 7 * * page 6, line 44-52; claims 3,4; figure 1 *	1,2,4-8	B01D53/14
X	EP 0 705 637 A (KANSAI ELECTRIC POWER CO ; MITSUBISHI HEAVY IND LTD (JP)) 10 April 1996 * page 5, line 41-45 *	1-4,6-8	
X	GB 2 167 397 A (SNAM PROGETTI) 29 May 1986 * page 1, line 89-102 * * page 2, line 60-69 * * page 2, line 109-113; figure 2 *	1-3,6-8	
A	US 4 406 868 A (CARTER CECIL O ET AL) 27 September 1983		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B01D
Place of search MUNICH		Date of completion of the search 28 June 1999	Examiner Polesak, H
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03 02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 10 5774

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28-06-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0558019 A	01-09-1993	DE 69306829 D	06-02-1997
		DE 69306829 T	15-05-1997
		DK 558019 T	14-04-1997
		KR 123107 B	12-11-1997
		JP 2871335 B	17-03-1999
		JP 5301024 A	16-11-1993
		JP 2871334 B	17-03-1999
		JP 5301023 A	16-11-1993
EP 0705637 A	10-04-1996	JP 8103630 A	23-04-1996
		JP 8252430 A	01-10-1996
		JP 8257354 A	08-10-1996
		JP 8257355 A	08-10-1996
		CN 1127156 A	24-07-1996
		EP 0880990 A	02-12-1998
		EP 0879631 A	25-11-1998
		EP 0880991 A	02-12-1998
		NO 953103 A	09-04-1996
GB 2167397 A	29-05-1986	US 5618506 A	08-04-1997
		AU 5005185 A	05-06-1986
		BR 8506058 A	19-08-1986
		DD 241015 A	26-11-1986
		DE 3541775 A	28-05-1986
		DK 544185 A	27-05-1986
		FR 2573671 A	30-05-1986
		JP 61136421 A	24-06-1986
		NL 8503265 A	16-06-1986
US 4406868 A	27-09-1983	SE 8505463 A	27-05-1986
		US 4741884 A	03-05-1988

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82